Atmospheric Emission of BDE-209 in Japan

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants used in a variety of products. Among the three commercial PBDE products, the deca-BDE product has the largest production volume. The deca-BDE product is dominated by the BDE-209 congener, which is widely detected in the environment[1-3]. Knowledge of their sources and emission inventories is important for the risk management of these compounds. Previous studies on the sources of PBDEs[4-6] are based on expert judgments and laboratory experiments rather than field measurements[7, 8]. Few studies[6, 9] have examined their estimated inventories by comparing the observed concentrations and the concentrations predicted in their inventory. The aim of this study is to estimate the emission inventory of BDE-209 in Japan and to compare the predicted and observed concentrations.

Methods

Emissions

The emission factors of BDE-209 during each stage of the PBDE product life cycle are summarized in Table 1. These factors were used to estimate the annual atmospheric emission of BDE-209 in Japan. The estimated emission ranged from 0.12 ton/year to 25 ton/year. Based on this result, three emission scenarios for the model evaluation were configured (Table 2). The emission in the middle scenario (1.7 ton/year) was set at the geometric mean of the emissions in the high scenario (25 ton/year) and in the low scenario (0.12 ton/year).

Table 1: Reported atmospheric emission factors of BDE-209 and the estimated emissions in Japan

Life stage	Emission factors		References	Activity		Emission (kg/year)
Production of DBDE	7.0E-05	-/-	ECB (2002) [5]	1,200 [a]	ton/year	84
Application to plastics	5.0E-04	-/-	ECB (2002) [5]	2,200 [b]	ton/year	1,100
	2.0E-04	-/-	ECB (2002) [5]	2,200 [b]	ton/year	440
	3.0E-07	-/-	Sakai et al. (2004) [7]	2,200 [b]	ton/year	0.66
Use of final product	3.8E-04	-/year	ECB (2002) [5]	60,000 [c]	ton	23,000
	1.0E-05	-/year	Alcock et al. (2003) [6]	60,000 [c]	ton	600
	2.0E-06	-/year	ECB (2002) [5]	60,000 [c]	ton	120
	3.2E-07	-/year	Danish EPA (1990) [4]	60,000 [c]	ton	19
Recycling/dismantling	2.0E-05	-/-	ECB (2002) [5]	6,000 [d]	ton/year	120
	3.0E-07	-/-	Sakai et al. (2004) [7]	6,000 [d]	ton/year	1.8
Incineration	1.0E-04	-/-	Danish EPA (1999) [4]	6,000 [d]	ton/year	600
	3.0E-06	-/-	JWRF (2002) [8]	6,000 [d]	ton/year	18
Total						120 - 25,000

a: Domestic production of DBDE in Japan in 1997. (Latest information available)
b: Domestic demand of DBDE in Japan in 2002. (Latest information available)
c: Cumulative domestic demand of DBDE in Japan from 1991 to 2000. Average lifetime of PBDE products (TVs and cars) is approximately 10 years.
d: Average domestic demand of DBDE in Japan in the 1990s.

Table 2: Model parameters

Symbol	Parameter			
SC	Scavenging coefficient	(1) 200,000 [14]		(2) 370,000 [12]
		(x)		(y)
log Koa	Octanol-air partition coefficient	11.822 [9]		15.27 [15]
log Kaw	Air-Water partition coefficient	-0.464 [9]		-5.07 [15]
T_{air}	Degradation half-life in air [h]	(L) 7,620 [9]		(S) 37 [11]
T_{soil}	Degradation half-life in soil [h]	(a) 530 [11]	(b) 3,600 [9]	(c) 30,000 [10] (d) Infinity
I_{air}	Atmospheric emission of BDE-209 in Japan [ton/year]	Low scenario	Middle scenario	High scenario
		0.12	1.7	25

Fate modeling and parameters settings
The mass balances of BDE-209 in air and soil are modeled as shown in eq. 1-4.

$$V_{air}\frac{dC_{air}}{dt} = I_{air} - \left[\phi\, v_{pdep} + \phi\, SC\, Rain + (1-\phi)\frac{Rain}{K_{aw}}\right] A\, C_{air} - \frac{\ln(2)}{T_{air}} V_{air}\, C_{air} - k_{adv}\, V_{air}\, C_{air} \quad \text{.....(1)}$$

$$W_{soil}\frac{dC_{soil}}{dt} = \left[\phi\, v_{pdep} + \phi\, SC\, Rain + (1-\phi)\frac{Rain}{K_{aw}}\right] A\, C_{air} - \frac{\ln(2)}{T_{soil}} W_{soil}\, C_{soil} \quad \text{.....(2)}$$

$$\phi = 1 - \frac{1}{1 + K_p\, TSP} \quad \text{.....(3)}$$

$$\log K_p = \log K_{oa} + \log f_{OM} - 11.91 \quad \text{.....(4)}^{13}$$

A: Contact area of air and soil = 377,887 × 10^6 [m^2]
V_{air}: Volume of air compartment = 377,887 × 10^9 [m^3]
W_{soil}: Weight of soil = 2 × 10^{16} [g-dry]
$k_{a\text{-}adv}$: Exchange rate of air by advection = 0.02 [1/h]
v_{pdep}: Dry particle deposition velocity = 10 [m/h]
Rain: Precipitation = 1.8 × 10^{-4} [m/h] (1.6 m/year)
TSP: Total suspended particle concentration = 50 [micro-g/m^3]
f_{OM}: Organic fraction of aerosol particles = 0.1 [kg/kg]
ϕ: Particle associated fraction of BDE-209 [g/g]
Kp: Particle-gas partition coefficient [m^3/micro-g]

The spatial scale used for the model was based on the area of Japan, that is, 378,000 km^2. The particle-associated fraction of BDE-209 in the air was estimated using Koa. The evaporation of BDE-209 from soil to air was treated as negligible. The atmospheric deposition of BDE-209 was assumed to be the single source of the congener to the soil. Several parameter-cases were used in case of some parameters to incorporate the uncertainty of these parameters into the model. Steady-state concentrations were calculated except for case (d) in which the half-life in soil was assumed to be infinite. In case (d), the concentration of BDE-209 in soil after 14 years of continuous atmospheric deposition was calculated. The period of 14 years is obtained by dividing the cumulative production of DBDE in Japan (84,000 ton) with the average annual production of DBDE in the 1990s (6,000 ton/year).

Monitoring data
The reported environmental levels of BDE-209 in Japan (air, atmospheric deposition, and soil) are summarized in Table 3.

Table 3: Reported concentrations of BDE-209 in Japan

Media	Unit	Average (median)	Range	*	References
Air	pg/m^3	10 (7.9)	0.80-34	18/19	MoE (2004, 2002) [1, 2]
Atmospheric deposition	$ng/m^2/day$	39 (21)	0.30-240	25/26	MoE (2004, 2002, 2001) [1-3]
Soil	ng/g	10 (0.40)	0.06-195	25/30	MoE (2004, 2002, 2001) [1-3]

*: Number of detection/number of samples

Results and Discussion

Atmospheric fate

The predicted gas phase fractions of BDE-209 in air were 20% (log Koa = 11.82) and 0.009% (log Koa = 15.27). Thus, most of the BDE-209 in air was predicted to be in the particle phase in both the parameter cases. The predicted atmospheric residence time ranged from 9 h to 17 h. In all parameter cases, the dominant elimination process from the air was deposition, followed by advection and decomposition (Fig. 1). The residence time was longer in case of (i) longer half-life in the air (case L), (ii) lower particle-phase fraction (case x), and (iii) lower scavenging coefficient (case 1).

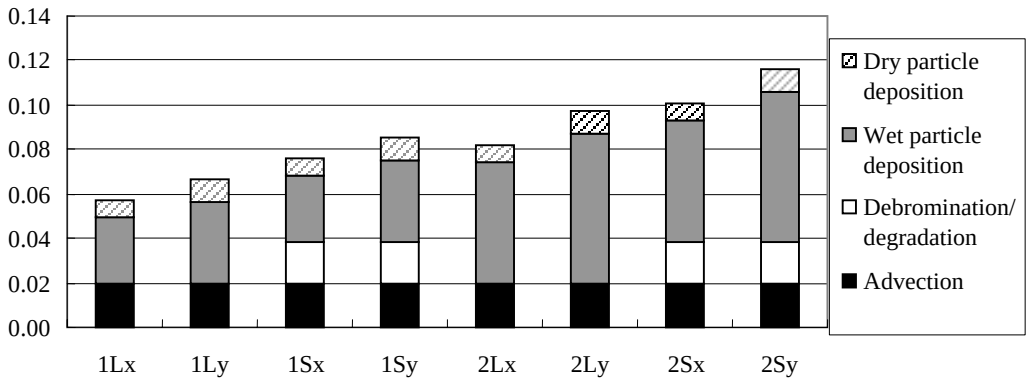
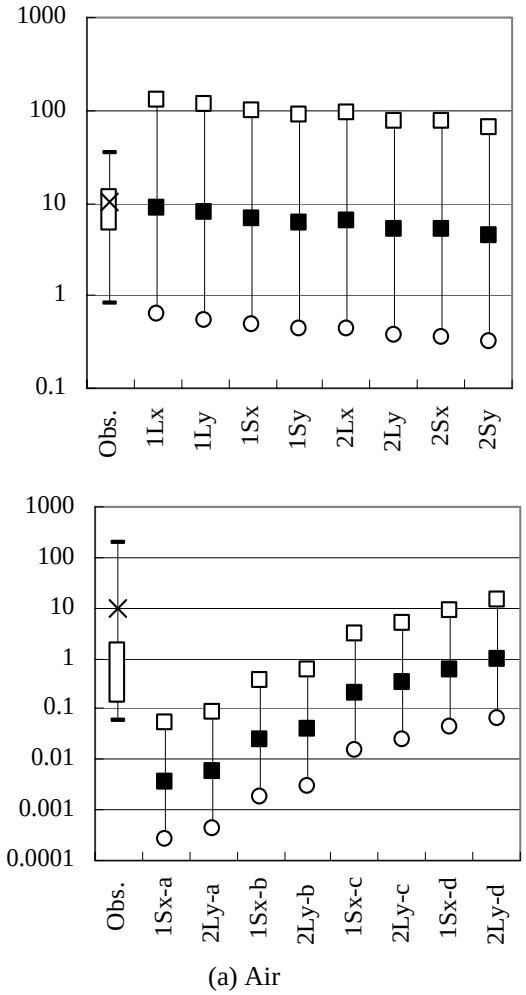


Fig. 1: Contribution of the elimination processes in the air [1/hr]. The inverse values of the Y axis correspond to the residence time of BDE-209 in the air.

Comparison of the predicted and observed BDE-209 concentrations in air and soil

In the high scenario (25 ton/year), the predicted concentrations in air of all parameter cases were higher than the highest concentrations observed in Japan's ambient air (Fig. 2a). In the low scenario (0.12 ton/year), the predicted concentrations in air of all parameter cases were lower than the lowest concentrations observed; the predicted concentrations in soil were lower or equal to the lowest concentrations observed (Fig. 2b). In the middle scenario (1.7 ton/year), the predicted concentrations in air were equal or slightly lower than the average and the median of the observed concentrations. As regards the soil, in the middle scenario, the predicted concentrations in case (c)

or (d), which assumed that the half-life in soil is longer than 30,000 h, were almost the same as the median of the observed concentrations but about ten times lower than the average of these observations. Considering the skewed distribution of the observed concentrations in soil affected by some extremely high values, the discrepancy between the average of the observation and the predicted concentrations in case (c) or (d) of the middle scenario is acceptable. These results suggest that the actual atmospheric emission of BDE-209 in Japan is lower than the high scenario (25 ton/year), higher than the low scenario (0.12 ton/year), and it could be slightly higher than the middle scenario (1.7 ton/year). We think that the most probable estimate for the BDE-209 emission is 3 ton/year and that the actual emission probably lies between 1 ton/year and 7 ton/year.



(a) Air (b) Soil

Fig. 2: Observed and predicted BDE-209 concentrations in air [pg/m^3] (left) and in soil [ng/g] (right). The arithmetic mean of the observations is denoted by "×." The minimum, maximum, 25th percentile, and 75th percentile of the observed concentrations are also shown. The white boxes

show the results for the high scenario (25 ton/year), black boxes for the middle scenario (1.7 ton/year), and the white circles for the low scenario (0.12 ton/year).

By examining the contribution of each product life stage to the emission estimate (Table 1), we can conclude that the emission factor for the use of the final product by ECB (2002) [5] is overestimated. On the other hand, the emission estimate for the sources based on field measurements (application to plastics, [7] recycling, [7] and incineration [8]) amount to only 0.02 ton/year, which is not sufficient to explain the current environmental levels in Japan. Further studies on the field measurements and emission factors of DBDE are necessary to fill the gap between our understanding of the environmental levels and the primary sources of this compound.

Acknowledgements
The authors are grateful for the financial support provided for this study by a Waste Management Research Grant: "Material Cycles Modeling of Persistent Toxic Chemicals and its Policy Research Applications for Recycling and Waste Management," from the Ministry of the Environment, Japan, in 2003.

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